EXHIBITS

U.S. Patent Nos.
1,992,325
2,259,453
2,407,543
3,034,806

Fig. 1

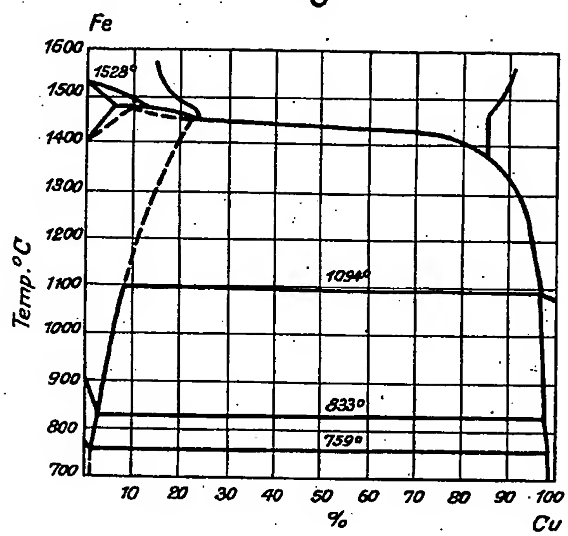
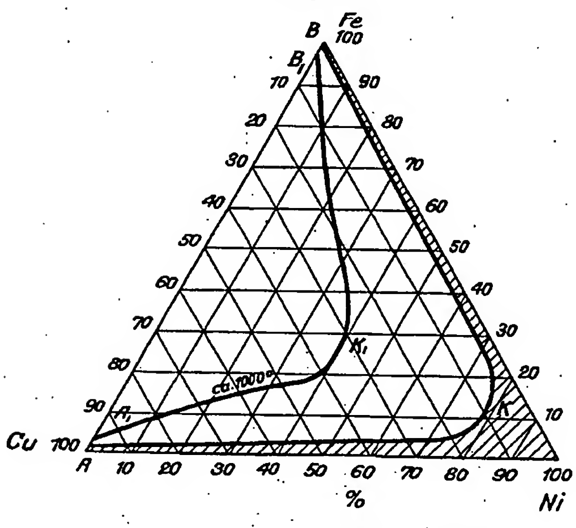


Fig. 2



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Feb. 26, 1935. C. SCHAARWÄCHTER 1,992,325

PROCESS OF NORMALIZING TERNARY AND MULTIPLE ALLOYS FORMING SOLID SOLUTIONS

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Fig. 3

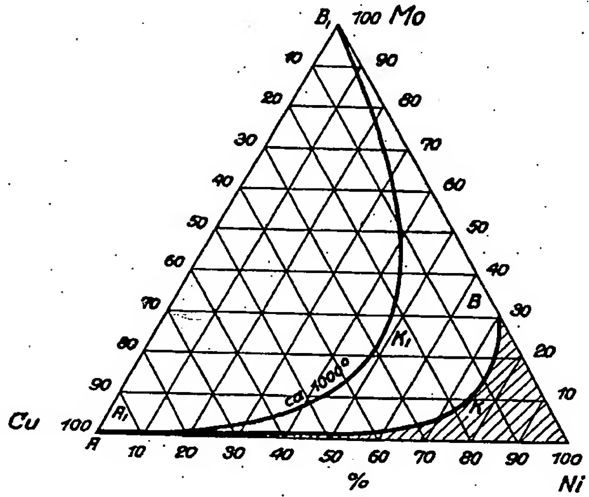
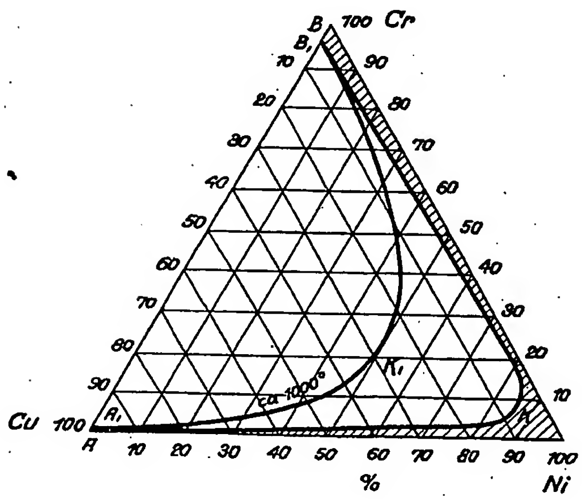


Fig. 4



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1,992,325

UNITED STATES PATENT OFFICE

1,992,325

PROCESS OF NORMALIZING TERNARY AND MULTIPLE ALLOYS FORMING SOLID SOLUTIONS

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10 Claims. (Cl. 148—11.5)

This invention relates to a process of normalizing ternary and multiple alloys forming solid solutions.

In the manufacture of alloys a number of normalizing methods are known, according to which the alloys are first heated at temperatures below the solidus curve, then quenched and aged at ordinary or elevated temperature. Of these normalizing processes the best known is that of Wilm according to which aluminium alloys, containing magnesium, and generally copper as well, are treated in this manner. Another similar process of normalizing copper alloys containing silicon by heat treatment has been brought out recently. All these processes are based upon the principle of effecting the formation of fine-grained compounds of the metals, either with the basic metal, or with an additional element within the range of the variable solubility (determined by the temperature) of the compound in the basic metal, by the heat treatment, and thereby improving the alloy.

The subject of the present invention is the technical utilization of the discovery, that in alloys with three and more components, changes in the degree of mutual solubility of the mixed crystals also take place, according to the temperature, if in the binary systems a gap exists in the miscibility of any two of the components, which gap can be completely or largely closed by the addition of a third element giving a complete or considerable formation of mixed crystals with each of the two first elements. This knowledge may be utilized in two ways,

Firstly, the present invention consists in converting a number of alloys with three or more components, hitherto regarded only as heterogeneous and not rollable, though possessing valuable qualities (for instance as to tenacity, hardness, resistance against corrosion etc.) into a condition, in which they become mechanically workable, and particularly rollable. Alloys of this kind can consequently be utilized for various industrial purposes, for which they were hitherto unsuitable.

Furthermore, the invention relates to a method of normalizing alloys of this kind within a certain range of composition, and thus also pointing out new ways of improving alloys which are already known.

It is a known fact, that systems with three or more components with a more or less completely closed gap in miscibility, can be obtained from metallic systems displaying gaps in miscibility, by the addition of an element, which produces a complete or considerable formation of mixed crystals with each of the participating metals, which show no or only a limited mutual solubility. Thus for example the copper-iron diagram shows a miscibility gap within wide limits (cf. for instance the solidification curves of this system by Ruer and Goerens "Ferrum" vol. 14, p. 49, in Fig. 1). By the addition of nickel, which produces a complete formation of mixed crystals with iron, as well as with copper, the miscibility gap can be almost completely closed. These conditions are explained by the system copper-nickel-iron in the accompanying diagram, Fig. 2. The line A K B divides the diagram into two parts, the one on the right containing every series of alloys with a homogeneous structure, and that on the left all those which under ordinary conditions possess a heterogeneous structure. Generally, the homogeneous alloys alone are considered to be well adapted for rolling. These are shown in the hatched part of the figure.

It has now been unexpectedly found, that the position of this line A K B, which separates the two parts, is a function of the temperature. This line which shows the stable conditions at the ordinary temperature, moves to the left, if the temperature rises, thereby diminishing the heterogeneous field. The heterogeneous field prevailing at 1000° C. is marked by the line A' K' B'. Accordingly the number of rollable alloys increases, as now those alloys which range between A K B and A' K' B' can also be made homogeneous by heating. The alloys homogenized in this manner can now be rolled at or below the homogenizing temperature, i. e. at temperatures above 800° C., or they can be quenched and then worked in the cold. The phase which is stable at the higher temperature is maintained at the ordinary temperature by quenching.

When test pieces first worked in a warm state and then quenched, or first quenched and then worked in the cold, were annealed at a temperature between 400 and 600° C., a further increase in hardness was unexpectedly attained. This shows, that alloys, the composition of which lies within the range of enlarged miscibility, can be normalized.

The existing literary statements regarding the system copper-nickel-iron (cf. especially the investigations by Vogel published in the "Zeitschrift für anorganische und allgemeine Chemie", vol. 67, 1910) suggest a position of the dividing line, between the homogeneous and heterogeneous field, which does not agree with the actual

facts, because a normalizing effect can be shown in the case of a number of those alloys which still belong to the field, which Vogel calls "homogeneous", by tempering them for a sufficiently long time.

The discovery on which the present invention is based affects not only the alloys of the copper-nickel-iron system, but also all systems of a similar structure.

Substituting the letters A, B and C for copper-nickel-iron, the following conditions have to be fulfilled:—

(*a*) The elements A and B must not form considerable quantities of mutual solid solutions; such systems being of special importance which are partially unmixable in the fluid state.

(*b*) The metal C must be able to form considerable quantities of mixed crystals, i. e. solid solutions, with the metal A as well as with the metal B, without however producing intermetallic compounds.

(*c*) Consequently the ternary system shows a dividing line, a homogeneous field being formed, i. e. a field in which complete miscibility of the three elements in the solid state exists.

In addition to the typical diagrams given above, the diagrams of, for example, the systems copper-nickel-chromium and copper-nickel-molybdenum also correspond to these conditions. In the above mentioned systems the nickel can be replaced by manganese; and iron, chromium, molybdenum, by cobalt, vanadium, tungsten or platinum. As illustrative examples, the systems copper-nickel-chromium and copper-nickel-molybdenum are given in the accompanying Figures 3 and 4.

In order to explain the practical importance of the invention, the improvements resulting from the developed method may be shown by the following example:—

An alloy, made of 34% of copper, 55% of nickel, 10.3% of chromium and containing a small amount of impurities, was rolled. It was found, that by rolling, the material developed flaws and was unsuitable for manufacturing purposes. The same alloy was then heated at 1100° C. until the structure became homogeneous, and was then quenched. The alloy now had a hardness of 136° Brinell and could be rolled very easily. After rolling, the hardness was 240° Brinell, and after subsequent heating to 400–600° C. the hardness was raised to 300° Brinell. When the material was heated to 700° C. directly after being quenched, without having been previously rolled, an increase of hardness from 136° to 200° Brinell was attained.

Quite independently of the working properties attained by homogenizing the test piece, which was heterogeneous at ordinary temperatures, it was unexpectedly found, that also by a second method of treating by heat, cold-working properties could be imparted; for when alloys of a composition within the range of enlarged miscibility are heated for a certain time to a temperature closely below that required for rendering them homogeneous, and thereafter cooled, test pieces made of these alloys proved highly suitable for rolling. No accurate scientific explanation of this phenomenon can be given with certainty. Probably the heterogeneous elements of the structure which, in the beginning were dispersedly separated, coalesce to larger globular aggregations. Thus the prolonged heating leads to the formation of a structure, which consists of two juxtaposed mixed crystals, and through the application of heat, has assumed a rollable form. Nevertheless the working can be carried to a much greater extent in the case of alloys which are in a state of homogeneity.

For example, an alloy containing 34% of copper, 8.2% of chromium, and 57.8% of nickel, was heated for 24 hours at 800° C. and then slowly cooled. The test pieces although having the comparatively high hardness of 170° Brinell, nevertheless were suitable for rolling.

Alloys produced according to the present invention, especially copper-nickel alloys with a high content of chromium exhibits very high resistance to corrosion; and admirably withstand the attacks of acids, lyes and other corrosive agents. They are therefore particularly suitable for the production of numerous articles, which are required to possess good workability, and tenacity, great hardness and high resistance to corrosion, such as, for instance, kitchen utensils, winding ropes, all kinds of needles, medical instruments, nozzles for the manufacture of artificial silk, marine cables, springs, hardened writing pens, electric resistance wires, piano strings, loom wires, valve-cones and rings, materials for bankers'-safes, spokes, highly stressed machine-parts and the like.

For the further improvement of certain properties of alloys, the fundamental composition of which corresponds with the described scheme, other components may be added. Thus for example, a small addition of carbon produces further hardening which renders the material suitable for the manufacture of knives. Other elements besides carbon, for example silicon or silver, may be added and the presence in the alloy of such other elements or materials which do not adversely affect the amenability to the treatment described is not to be understood as a departure from the invention.

Moreover, it is within the scope of the invention to add to the compositions defined in the appended claims minor amounts of manganese, molybdenum, tungsten and/or vanadium without materially displacing the lines A K B and A' K' B' in the accompanying drawings.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. A process for manufacturing workable alloys consisting of copper, nickel and one metal of the group consisting of iron and chromium, in amounts such that the compositions are outside the normal range of miscibility at ordinary temperatures but are within the range of miscibility at temperatures approaching the melting points of the alloys, which comprises homogenizing the alloys by heating the same at a temperature between about 800° C. and the melting points of the alloys, and thereafter mechanically working them.

2. A process for manufacturing workable alloys as defined in claim 1, characterized in that the alloys after homogenizing heating are quenched and then mechanically worked.

3. A process for manufacturing workable alloys as defined in claim 1, characterized in that the alloys after homogenizing heating are first mechanically worked while at an elevated temperature and then are quenched.

4. A process for manufacturing workable alloys as defined in claim 1, characterized in that the alloys after homogenizing heating and mechanical working are tempered at a temperature between about 300° and 800° C.

5. A process for manufacturing workable alloys consisting of copper, nickel and iron in amounts lying within the field defined by curves A K B and A' K' B' in the diagram represented by Figure 2 of the accompanying drawings which comprises heating said alloys at a temperature between about 800° C. and the melting point of the alloys and thereafter mechanically working the alloys.

6. A process for manufacturing workable alloys as defined in claim 5, characterized in that the alloys after the heat treatment are quenched and then mechanically worked.

7. A process for manufacturing workable alloys as defined in claim 5, characterized in that the alloys after the heat treatment are quenched and mechanically worked, and finally are tempered at a temperature between about 300° and 800° C.

8. A process for manufacturing workable alloys consisting of copper, nickel and chromium in amounts lying within the field defined by curves A K B and A' K' B' in the diagram represented by Figure 4 of the accompanying drawings which comprises heating said alloys at a temperature between about 800° C. and the melting point of the alloys and thereafter mechanically working the alloys.

9. A process for manufacturing workable alloys as defined in claim 8, characterized in that the alloys after the heat treatment are quenched and then mechanically worked.

10. A process for manufacturing workable alloys, as defined in claim 8, characterized in that the alloys after the heat treatment are quenched and mechanically worked and finally are tempered at a temperature between about 300° and 800° C.

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